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Harrad, Stuart; Drage, Daniel; Sharkey, Martin; Berresheim, Harald

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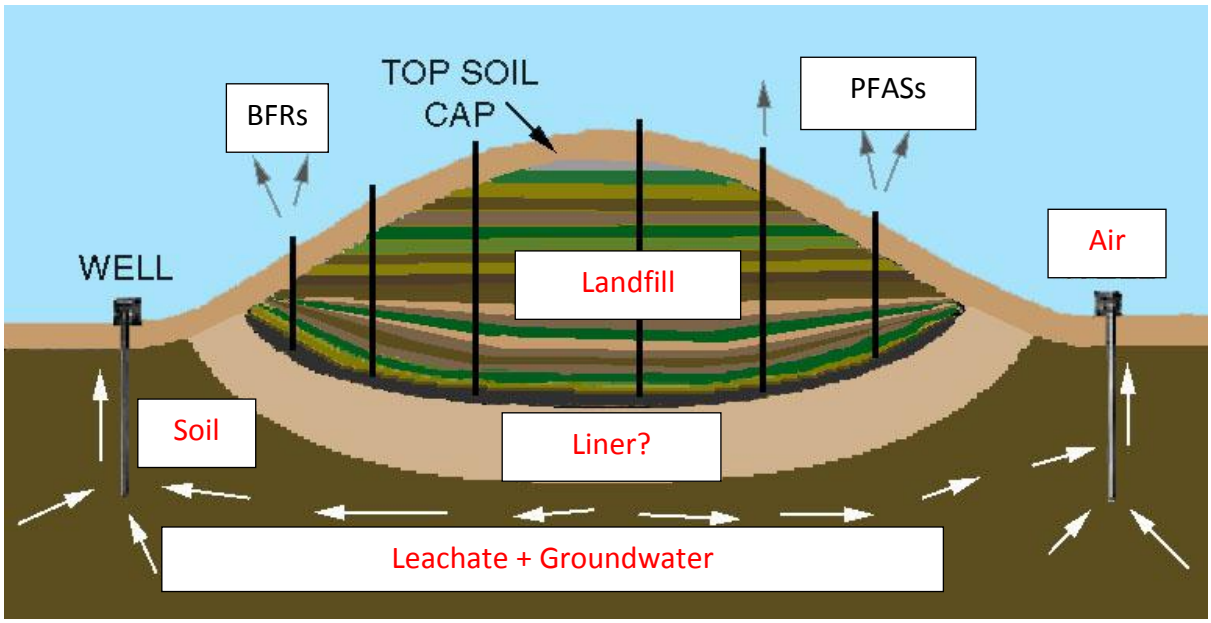
*Graphical Abstract



HIGHLIGHTS

- BFRs and PFASs measured in air, soil and groundwater near 10 Irish landfills
- First report of DBDPE in groundwater at levels exceeding PBDEs, HBCDD and PFOA
- BFRs and PFASs in air and soil not impacted by landfill
- PFOA in groundwater positively correlated with concentrations in landfill leachate
- PFOA higher in groundwater near unlined than near lined landfills

Perfluoroalkyl Substances and Brominated Flame Retardants in Landfill-Related Air, Soil, and Groundwater from Ireland

Stuart Harrad* [a], Daniel S Drage[a], Martin Sharkey[b], Harald Berresheim[b]

[a] School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK

[b] School of Physics, National University of Ireland Galway, Galway, Ireland

*Corresponding Author

S.J.Harrad@bham.ac.uk

ABSTRACT

Between November 2018 and January 2019, samples of air and soil were collected from locations downwind and upwind of 10 landfills across the Republic of Ireland. Samples of groundwater (n=10) were also collected from locations with links traceable to the studied landfills. Concentrations of perfluoroalkyl substances (PFASs), polybrominated diphenyl ethers (PBDEs), hexabromocyclodecane (HBCDD), and decabromodiphenyl ethane (DBDPE) determined in air and soil samples were not significantly different ($p>0.05$) between downwind and upwind locations. The arithmetic mean concentration of PFOA in groundwater sourced from landfills (n=4) that were not fully lined (69 ng/L) exceeded that in groundwater samples sourced from lined landfills (n=6; 4.1 ng/L), with the difference, however being not statistically significant ($p>0.1$). A positive correlation ($p=0.014$) was observed between concentrations of PFOA in groundwater in our study and those reported previously in leachate from the same landfills. However, this correlation was driven substantially by one landfill which displayed the highest concentrations in both groundwater and leachate and no significant correlation ($p>0.1$) was observed between log-transformed concentrations of PFOA in groundwater and leachate. DBDPE was detected in groundwater for the first time anywhere, in all samples at concentrations (median = 9.4 ng/L; arithmetic mean = 78 ng/L) that exceeded those of any other BFRs or PFASs targeted in this study. This likely reflects its recent use as a "drop-in" replacement for the recently restricted Decabromodiphenyl ether product. Overall, our data suggest that the 10 landfills studied do not exert a discernible influence on local air and soil concentrations of BFRs and PFASs. In contrast, while not of immediate concern, our data suggest that further more detailed study of the impact of landfill emissions on concentrations of DBDPE and PFOA is advisable.

KEYWORDS

PFASs; BFRs; DBDPE; Landfill; Air: Soil; Groundwater

HIGHLIGHTS

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- First report of DBDPE in groundwater at levels exceeding PBDEs, HBCDD and PFOA
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INTRODUCTION

Perfluoroalkyl substances (PFASs) have found widespread application in domestic, institutional, and office environments to for example confer stain/oil repellency to fabrics and food packaging (BiPRO, 2011, Miralles-Marco and Harrad, 2015). Similarly, brominated flame retardants (BFRs) like polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have been used extensively in a broad range of applications such as soft furnishings and fabrics, as well as electrical and electronic equipment (BiPRO, 2011). Concerns about their adverse impacts on human and wildlife health have led to restrictions and bans on the manufacture and use of PBDEs, HBCDD, and PFASs like perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), exemplified by their listing or (in the case of perfluorohexane sulfonate (PfHxS)) active current consideration for listing under the

61 Stockholm Convention on persistent organic pollutants. Despite such concerns, there
62 remain a substantial quantity of articles treated with such chemicals (Drage et al,
63 2018). One consequence of such restrictions has been increased use of alternative
64 flame retardants and PFASs, as evidenced by our recent reports of elevated
65 concentrations of decabromodiphenyl ethane (DBDPE) and perfluorobutane sulfonate
66 (PFBS) in indoor air and dust from Ireland (Harrad et al, 2019b; Wemken et al, 2019).
67 As articles containing BFRs and PFASs become redundant, they enter the waste
68 stream. One widely-favoured waste disposal method has historically been landfill.
69 While disposal of waste electrical and electronic equipment (WEEE) to landfill has
70 been restricted since 2003 within the European Union (EU) as a result of the WEEE
71 directive (EC, 2003); similar restrictions on landfilling of waste soft furnishings and
72 fabrics do not exist and moreover, landfills located within the EU that were open
73 before 2003 may contain WEEE received before this date. Given such material may
74 contain elevated concentrations of PBDEs, HBCDD, and PFASs; its presence in
75 landfill is of potential concern.
76 We recently reported on the ubiquitous presence of PBDEs, HBCDD, and a number
77 of PFASs in leachate from 40 landfills in the Irish Republic (Harrad et al, 2019a). We
78 also reported that concentrations of some BFRs and PFASs were significantly higher
79 in leachate from landfills fitted with impervious liners than in leachate from landfills
80 that were partially or completely unlined. This was attributed to the higher organic
81 matter content of leachate from lined landfills (Harrad et al, 2019a), and raised
82 concern that BFRs and PFASs in leachate from unlined landfills could potentially
83 contaminate groundwater. Additional concerns have also been voiced that
84 volatilisation of PBDEs and PFASs from landfilled waste may lead to elevated

concentrations in air in the vicinity of landfills (St. Amand et al, 2008; Weinberg et al, 2012).

This study tests the hypothesis that landfills have caused discernible contamination of their surrounding environment. To do so, we report concentrations of PBDEs, HBCDD, DBDPE, and PFASs in samples of air and soil taken both down-and up-wind of 10 landfills in the Republic of Ireland. We also report concentrations of the same contaminants in samples of groundwater linked to the same landfills. In addition to facilitating assessment of the influence of landfills on the surrounding environment, the data reported here represent the most detailed database yet on these contaminants in Irish groundwater, outdoor air, and soil.

MATERIALS AND METHODS

Sampling

Air and soil - Air and soil samples were collected between 6th November 2018 and 31st January 2019 from 10 municipal solid waste (MSW) landfill sites across the Republic of Ireland (Figure 1). A summary of the methods employed is provided here, with further information about the sampling locations and factors like the passive air sampling rates used to calculate concentrations in air samples (taken from Drage et al, 2016 and Goosey and Harrad, 2012) provided as supporting information.

Each passive air sampler deployed consisted of a polyurethane foam (PUF) disk (140 x 140 x 12 mm) mounted between two stainless steel bowls lined with hexane-rinsed aluminium foil. Each PUF disk was coated with pre-cleaned Amberlite XAD powder by submerging each disk in a solution of the powder crushed to a particle size of 0.75 μm suspended in hexane. Once dried, the disks were loaded into the passive air samplers, two of which were placed at locations upwind and downwind, respectively,

109 of each landfill site. The locations of sampling sites were based on wind direction data
110 taken from the Irish Meteorological Service (Met Eireann), with slight modification
111 where necessary based on local information from the site operators and ease of
112 access. Sampling points were located between 150 and 500 m of the centre of the
113 landfill.
114 To maximise the effective air volume collected from each location for analysis, two
115 samplers were placed at each sampling point, hung either side of a fence post at a
116 height of 1.2 m above the ground, and left in place for approximately 2 months. At the
117 end of this period, the PUF disks were collected, sealed in a piece of hexane-rinsed
118 aluminium foil and placed in plastic ziplock bags for transportation to the University
119 of Birmingham for analysis.
120 Soil samples were also collected both upwind and downwind of the main landfill
121 body, in the same area as the air samples were taken. These samples were taken
122 within the boundaries of the landfill operational facility, but with care taken to avoid
123 sampling soil used as capping on landfill cells to ensure (i) that soil samples were not
124 collected from soil placed *after* landfill operations ceased, and (ii) that farming
125 activities would not influence concentrations of target compounds found.
126 Nine sub-samples of soil (100 g each) were taken from each downwind and upwind
127 sampling location, in a "W" formation, with each sub-sample 10 m apart, using a
128 small pre-cleaned stainless steel shovel. For each 100 g sub-sample, the overlaying
129 foliage was removed from a circular area with a diameter of 10-15 cm. A cylinder of
130 soil, 10-15 cm wide and ~5 cm deep was loosened and homogenized, and a ~100 g
131 sub-sample of soil removed. This was repeated for each of the nine sub-sampling
132 points before each sub-sample was homogenised into a single sample in an amber
133 glass jar, sealed and then transported to the University of Birmingham. On receipt in

Birmingham, samples were air-dried in a fume hood at ambient temperature and homogenised further before an aliquot was removed for analysis.

Groundwater - Groundwater samples were collected from each of the ten sites from two sampling points down-gradient from the main body of the landfills (per landfill zoning maps information). Each sampling point consisted of an approximately 5 cm wide borehole leading down to water reservoirs at a minimum depth of 5 m below ground level. A number of such sampling points are present at every Irish landfill to facilitate quarterly monitoring of water quality by the Irish Environmental Protection Agency. Samples were manually pumped and collected using clean polyethylene tubes and a foot-valve (allowing for the one way flow of water through the tube). Approximately 25 L of water were purged from each of the two sampling points per landfill, before a 500 mL sample was collected in a pre-cleaned polystyrene bottle. The two samples taken per landfill were then combined into a single 1 L pre-cleaned polystyrene bottle, with this combined sample used for analysis. Following transfer to the laboratory, each combined sample was split, with one half analysed for BFRs (passed through a glass fibre filter (GFF) and PUF before extraction) and the other for PFASs (subjected to solid phase extraction (SPE)).

Target analytes – The following BFRs and PFASs were targeted in this study: PBDEs 28, 47, 99, 100, 153, 154, 183, and 209; α–, β- and γ-HBCDD, DBDPE and PFOS, perfluorobutane sulfonate (PFBS), PFHxS, PFOA, perfluorononanoic acid (PFNA), perfluoro-1-octanesulfonamide (FOSA), N-methylperfluoro-1-octanesulfonamide (MeFOSA), N-ethylperfluoro-1-octanesulfonamide (EtFOSA), 2-(N-methylperfluoro-

158 1-octanesulfonamido)-ethanol (MeFOSE), and 2-(N-ethylperfluoro-1-
159 octanesulfonamido)-ethanol (EtFOSE).
160
161 *Sample Extraction*
162 Air Samples - For air samples, extraction and extract purification was carried out in
163 line with previously published procedures used to determine concentrations of the
164 same target BFRs and PFASs in Irish indoor air (Wemken et al, 2019; Harrad et al,
165 2019). Briefly, PUFs and GFFs were packed into 66 mL extraction cells and spiked
166 with known masses of internal standards (BDE-77, BDE-128, $^{13}C_{12}$-BDE-209, $^{13}C_{12}$-
167 α-HBCDD, $^{13}C_{12}$-β-HBCDD, $^{13}C_{12}$-γ-HBCDD, M8PFOS, M8PFOA, M8FOSA,
168 MPFHxS, MPFNA, d-N-MeFOSA, and d-N-EtFOSA (Wellington Laboratories,
169 Canada)). Where possible, native PFASs and BFRs were quantified relative to the
170 corresponding isotopically-labeled internal standard. Where this was not possible,
171 BDEs- 28, 47, 99, and 100 were quantified against BDE-77, BDEs- 153, 154, and 183
172 where quantified relative to BDE-128, while DBDPE was quantified using $^{13}C_{12}$-
173 BDE-209. For PFASs, PFBS, EtFOSA, and EtFOSE were quantified relative to
174 MPFHxS, d-N-MeFOSA, and d-N-MeFOSE respectively. Each cell underwent
175 sequential extraction to produce a BFR fraction followed by a PFAS fraction using a
176 Dionex ASE 350. The BFR fraction was obtained using hexane:DCM (3:1, v/v ratio)
177 as the extraction solvent, while the PFAS fraction was obtained with acetone. Both
178 were extracted at 90 °C with 5 minutes static time, 3 static cycles and 40% flush
179 volume. Crude extracts were concentrated to ~0.5 mL in hexane using a Turbovap II
180 (Biotage).
181 Groundwater – To determine concentrations of BFRs in groundwater, samples (0.5 L)
182 were first subjected to filtration via gravity sequentially through a GFF, followed by a

183 PUF cylinder (Harrad et al, 2009). Following filtration and air-drying in a fume hood,
184 the GFF and PUF from each groundwater sample were treated with BFR internal
185 standards and subjected to pressurised liquid extraction as per air samples. In contrast,
186 PFASs were extracted from groundwater samples using solid phase extraction.
187 Briefly, 0.5 L groundwater was spiked with known quantities of PFAS internal
188 standards and passed through an Oasis-WAX cartridge (150 mg/ 6 mL). Cartridges
189 were then dried under vacuum for approximately 30 minutes before target PFASs
190 were eluted with 6 mL methanol (0.1% NH_4OH).
191 Soil – BFRs were extracted from soils following spiking with internal standards, by
192 loading into an ASE cell and extracting as described for air samples. PFASs were
193 extracted from soil samples using ultrasonication. To summarise, 1 g of sample was
194 accurately weighed into a test tube, treated with internal standards and 7 mL of
195 methanol (0.1% NH_4OH) added. Samples were vortexed for 2 minutes followed by 30
196 minutes of ultrasonication at 20 °C. The tubes were centrifuged for 5 minutes at 3500
197 RPM and the supernatant collected into a new tube. The procedure was repeated twice
198 further and the three extracts were combined and concentrated to ~0.5 mL under a
199 gentle stream of nitrogen at 35 °C.
200
201 *Clean-up* – for BFRs in all matrices, extracts were diluted to ~2 mL in hexane, added
202 to 2 mL >95% concentrated sulfuric acid and vortexed for 2 minutes. The two layers
203 were separated by centrifugation at 3500 RPM for 5 minutes and the supernatant was
204 collected and concentrated to ~0.5 mL. Extracts were further purified by transferring
205 onto a preconditioned (6 mL DCM, 6 mL hexane) ENVI-Florisil SPE cartridge (500
206 mg/ 3 mL, Sigma Aldrich). Target BFRs were eluted with 6 mL hexane followed by 6

mL DCM. Clean extracts were concentrated to incipient dryness and reconstituted in 200 µL in toluene and transferred to autosampler vials ready for analysis.

For PFASs, extracts were purified by loading onto an ENVI-Carb (3 mL/250 mg, Sigma Aldrich) SPE cartridge. PFASs were eluted with 2 mL of methanol (0.1% NH_4OH) and concentrated to ~0.5 mL. Extracts were passed through a 0.22 µm polyether sulfone (PES) syringe filter, concentrated to 200 µL and transferred to autosampler vials ready for analysis.

Instrumental Analysis

DBDPE and PBDEs -28, -47, -99, -100, -153, -154, -183, and -209 were analysed on a Thermo TRACE 1310 GC coupled to a Thermo ISQ MS as described in Abdallah et al. 2017). HBCDDs (α-, β- and γ-) were analysed on an LC-MS/MS system composed of a Shimadzu LC-20AB Prominence liquid chromatograph coupled to an ABS Sciex API 2000 triple quadrupole mass spectrometer operated in negative ion mode. Full details are provided elsewhere (Abdallah et al. 2008).

PFASs (PFOA, PFOS, PFNA, PFHxS, PFBS, FOSA, EtFOSA, MeFOSA, EtFOSE, MeFOSE) were analysed in accordance with the procedures described in Harrad et al (2019a; 2019b) on a Sciex Exion HPLC coupled to a Sciex 5600+ triple TOF MS. Ten microliters of extract were injected onto a Raptor C18 column (1.8 µm particle size, 50 mm length, 2.1 mm internal diameter, Restek). Full details of the method including acquisition parameters and HPLC conditions are provided in the supporting information.

232 *Determination of total organic carbon (TOC) in soil samples*

233 TOC was determined in the soil gravimetrically by measuring the loss on ignition
234 after heating the dried samples at 500 °C for four hours. A clean crucible was
235 accurately weighed and the weight recorded (W1). One gram of the soil sample was
236 added to the crucible before being placed in an oven at 105 ºC for 24 hours to remove
237 all moisture and the weight recorded again (W2). The crucible was then placed in an
238 oven at 500 °C for 4 hours and left to cool before the weight of the crucible was
239 recorded a final time (W3). TOC was then determined using the following equation:
240

$$TOC\ (\%) = \frac{(W2 - W3)}{(W2 - W1)} \times 100$$

241 *Quality Control*

242 All samples were processed using procedures that have been previously validated
243 (Harrad et al., 2009, Gallen et al. 2016, Drage et al. 2016). For ongoing accuracy of
244 analysis of BFRs an aliquot of SRM-2585 (NIST) was analysed with every batch of
245 samples (n=4). For PFAS, SRM-2585 was also used for soil and air samples (n=4)
246 while a MilliQ sample spiked with target compounds was also analysed with each
247 batch of groundwater samples (n=2). All target analytes were found to be within 80-
248 120 % of their certified or spiked values, with less than 15% relative standard
249 deviation. Further information can be found in the Supporting Information.
250

251 Two field blanks comprising distilled deionised water sampled from the same
252 polystyrene groundwater collection bottles were analysed in identical fashion to
253 groundwater samples. For air samples, clean PUFs were used as field blanks (n = 2),
254 while for soil, clean anhydrous sodium sulfate (n = 2) was the field blank.
255 Concentrations of all target compounds (except for BDE-209) were below detection

limits in all blanks. Therefore with the exception of BDE-209, the method limits of detection were based on the compound mass generating a signal to noise ratio of 3:1. While BDE-209 was detected in all blank samples, this was only at an average of 7 pg/sample (± 1 pg/sample), which gave a signal to noise (S/N) ratio of 3:1. Therefore, method limits of quantification for all target compounds were estimated based on a S/N ratio of 10:1.

Statistical analysis

Descriptive statistics, t-tests and Pearson's correlation analyses were calculated using Excel for Mac v.16.28, while Wilcoxon Signed Rank tests were conducted using SPSS for Mac v.25.

RESULTS AND DISCUSSION

Concentrations of PBDEs, HBCDDs, and PFASs in Landfill-Related Air and Soil Samples

Background information about the landfills in this study is provided in Table SI-1. In summary, all of the landfills in this study primarily accepted municipal solid waste, along with some biomedical, non hazardous industrial, and construction and demolition waste. None of the landfills are located near any potential industrial sources of our target compounds. A full list of concentrations of all target PBDEs, HBCDDs, and PFASs in each individual air, groundwater, and soil sample is provided in supporting information (Tables SI2-SI7 inclusive). It is important to acknowledge that all samples were collected over the late autumn/winter period during which temperatures are lower. It is plausible that sampling in warmer periods of the year

would lead to higher concentrations in air due to enhanced volatilisation of our target compounds. Further monitoring in spring and summer months would thus be advisable to verify whether this is the case.

Air - Table 1 summarises concentrations of BDE-47, BDE-209, ΣHBCDD, and selected PFASs detected in samples of air from locations both downwind and upwind of the landfills in this study, alongside those from other relevant studies. DBDPE was only detected above its LOQ of 0.9 pg m^{-3} in one air sample taken downwind of a landfill (2 pg m^{-3}). To our knowledge, these are the first reported data on concentrations of PFASs in Irish outdoor air, and represent a very substantial addition to the measurements of PBDEs and HBCDD made at the background Malin Head site as part of the GAPS study (Lee et al, 2016; Rauert et al, 2018). Comparison of our data with those for Malin Head suggest concentrations of BDE-209 and HBCDD around the landfills studied here exceed slightly those at Malin Head. Concentrations of PBDEs, DBDPE, and HBCDD in the vicinity of Irish landfills are well below those reported recently for indoor air in Ireland (Wemken et al, 2019). For BDE-47, concentrations in the current study are lower than those reported previously in the UK, Sweden, Germany, and the USA (Drage et al, 2016; Hoh and Hites, 2005; Newton et al, 2015; Weinberg et al, 2011). With respect to BDE-209, our concentrations exceed those reported for Sweden (Newton et al, 2015), but are markedly lower than those detected in the UK and the USA (Drage et al, 2016; Hoh and Hites, 2005). Meanwhile, concentrations of HBCDD in this study are lower than in the UK (Drage et al, 2016), Sweden (Newton et al, 2015), and the USA (Hoh et al, 2005).

Concentrations of all our target PFASs in this study are substantially lower than those reported recently for indoor air in Ireland (Harrad et al, 2019). PFOA was detected at

higher concentrations in this study than in the UK (Goosey and Harrad, 2012), at both landfill and reference locations in Germany (Weinberg et al, 2011), and in Canada (Shoeib et al, 2011). This is consistent with our recent report that concentrations of PFOA in Irish indoor air exceed those reported elsewhere (Harrad et al, 2019b) and combined, these observations suggest extensive use of PFOA in Ireland. In contrast, concentrations of PFOS and PFHxS in this study are lower than those reported in outdoor air at a number of UK locations (Goosey and Harrad, 2012). Moreover, concentrations of PFOS, PFNA, PFBS, and PFHxS in this study are all within a similar range to those reported at landfill and reference (i.e. non-landfill-impacted) locations in Germany (Weinberg et al, 2011).

Soil – Concentrations of HBCDD, selected PBDEs and PFASs in soil from locations both down- and up-wind of Irish landfills are summarised in Table 2. Similar to air, DBDPE was detected above its LOQ of 250 pg g^{-1} (dry weight) in only one sample taken downwind of a landfill (540 pg g^{-1} dry weight). To the best of our knowledge, our study is the first to report concentrations of our target contaminants in Irish soil and may be the first report of concentrations in soil anywhere for PFBS. To aid comparison with relevant previous studies for PBDEs and HBCDD, data are provided both on a soil dry weight basis as well as normalised to soil organic matter content. Compared to landfill-impacted locations in northern Canada (Danon-Schaffer, 2010), dry weight concentrations in the current study of BDEs- 47, 99, 153, 183, and 209 are approximately one to two orders of magnitude lower. Instead, concentrations in this study resemble more closely those reported by Danon-Schaffer (2010) for soil from reference (non-landfill-impacted) locations in northern Canada. Other pertinent comparisons for PBDEs and HBCDD are with organic matter-normalised

330 concentrations reported for various locations along rural-urban transects in both the
331 UK (Drage et al, 2016) and Sweden (Newton et al, 2015). Overall, concentrations in
332 our study are broadly consistent with those in these earlier surveys.
333 With respect to PFASs, consistent with our observations for air, dry weight
334 concentrations of PFOA in our study are at the high end of the range previously
335 reported for various locations in Europe and North America (Goosey, 2010; Groffen
336 et al, 2019; Rankin et al, 2016). In contrast, concentrations of PFOS, PFNA, and
337 PFHxS in our soils are at the low end of the range of concentrations previously
338 reported. While our data appear the first report of PFBS in soil from non-industrial
339 locations, our concentrations are around 3 orders of magnitude below those reported
340 in the vicinity of a fluorochemical industrial park in China (Bao et al, 2019).
341 *Groundwater* – Table 3 summarises the concentrations of HBCDD, selected PBDEs,
342 and PFASs detected in samples of groundwater in this study, with data from
343 comparable studies elsewhere provided for reference. As far as we can ascertain, our
344 data are the first anywhere to report concentrations of both HBCDD and DBDPE in
345 groundwater. We detected DBDPE in all 10 groundwater samples analysed at median
346 and arithmetic mean concentrations that exceeded those of any of the other
347 contaminants measured in this study. While we did not measure DBDPE in a previous
348 study of leachate from Irish landfills (including some of those monitored here), our
349 observations in groundwater are consistent with our recent report of elevated
350 concentrations of DBDPE in indoor air and dust in Ireland (Wemken et al, 2019).
351 This suggests strongly that use of DBDPE is more substantial than thought hitherto,
352 likely as a “drop-in” replacement for the Deca-BDE formulation.
353 As expected, PBDE concentrations in our groundwater samples were lower than those
354 reported previously to be present in leachate from Irish landfills (Harrad et al, 2019a).

355 Moreover, our concentrations of PBDEs are lower than those reported previously for
356 groundwater from Canada and Taiwan (Levison et al, 2012; Trinh et al, 2019).
357 Turning to PFASs, our concentrations in groundwater are well below those reported
358 in Irish landfill leachate (Harrad et al, 2019a), but fall within a similar range to those
359 reported for Irish tapwater (Harrad et al, 2019b). Consistent with the predominance of
360 PFOA in air and soil observed in this study, PFOA is the dominant PFAS of those
361 targeted here, being the only PFAS detected in all samples and at concentrations
362 exceeding those of other PFASs. Compared to other studies of PFASs in groundwater,
363 the concentrations of PFOS, PFBS, and PFHxS reported here for Ireland are all at the
364 low end of previous reports for Japan and various European locations (Atkinson et al,
365 2008; Loos et al, 2010; Murakami et al, 2009; Weiss et al, 2012). In contrast, while
366 concentrations in Irish groundwater of PFOA are within the range reported for Japan,
367 Germany, and the UK (Atkinson et al, 2008; Murakami et al, 2009; Weiss et al,
368 2012); they appear higher than those measured in well water from the Netherlands
369 (Eschauzier et al, 2013) and a survey of various EU locations (Loos et al, 2010).
370 While we are unaware of previous reports of FOSA in European groundwater, the
371 concentrations we report here are consistent with those measured previously in Japan
372 (Murakami et al, 2009).

373 **Downwind and upwind concentrations of HBCDD, PBDEs, and PFASs in air**
374 **and soil in the vicinity of Irish landfills**

375 *Air* – Table 1 shows that with the exception of HBCDD, arithmetic mean and median
376 concentrations of all target compounds were higher at downwind locations than
377 upwind. To evaluate whether there was a statistically significant increment at sites
378 downwind of the landfills in this study, we compared downwind and upwind
379 concentrations of HBCDD, PBDEs and PFASs at our 10 landfills using a non-

parametric Wilcoxon signed-rank test. This revealed that downwind and upwind concentrations were statistically indistinguishable ($p>0.1$).

Soil – To evaluate whether there was any statistically significant difference between concentrations (expressed both as dry- and organic carbon-normalised weight) of our target contaminants in soil from the 6 landfills for which we had samples from both downwind versus upwind locations, we employed a non-parametric Wilcoxon signed rank test. This showed no significant difference between downwind and upwind locations ($p>0.1$).

Overall, our findings suggest no discernible impact of the landfills studied here on concentrations of HBCDD, PBDEs, DBDPE, and PFASs in air and soil surrounding these facilities. This is consistent with the data on concentrations of a similar range of contaminants measured in air in the vicinity of landfills in Germany (Weinberg et al, 2011) but appears in contrast with the data of Danon-Schaffer (2010) who detected markedly higher concentrations of PBDEs in soil around landfills in northern Canada than in reference locations.

Influence of landfill lining status on concentrations of HBCDD, PBDEs, and PFASs levels in groundwater

To minimise contamination by landfill leachate of the surrounding environment including groundwater; modern landfills are fitted with an impervious polymeric liner. In contrast, some older landfills have been operated unlined. In addition, some landfills (categorised here as "mixed") that were in operation before the use of such liners, remained open but were retrospectively equipped with new waste cells that were fitted with liners. In our previous study of Irish landfill leachate, we reported that concentrations of some BFRs and PFASs in leachate from lined landfills exceeded those in leachate from unlined landfills – as the liners are designed to retain

405 such contaminants within the landfill, and prevent their leaching into the environment
406 (Harrad et al, 2019a). This is supported by the fact that only the unlined (n=1) and
407 mixed (n=3) landfills in this study, release leachate to groundwater. We therefore
408 hypothesised that groundwater impacted by unlined landfills may contain relatively
409 higher concentrations of BFRs and PFASs. To test this hypothesis, we used a t-test to
410 compare concentrations of our target contaminants in groundwater sampled near the 6
411 lined landfills with those in groundwater obtained close to the 1 unlined and 3 mixed
412 landfills in this study. This revealed no significant difference ($p>0.1$) in
413 concentrations between groundwater from lined and mixed/unlined landfills.
414 However, we note our small sample size, that for PFOA $p=0.12$, and that arithmetic
415 mean concentrations of PFOA in groundwater from lined and mixed/unlined landfills
416 were 4.1 and 69 ng/L respectively.

417 **Relationship between concentrations of HBCDD, PBDEs, and PFASs in**
418 **groundwater and landfill leachate**

419 We examined our data on BFR and PFAS concentrations in groundwater in this study
420 for any correlation with those we recorded in leachate from the same 10 landfills in
421 our earlier study (Harrad et al, 2019a). Note that DBDPE was not measured in
422 leachate. We observed only one significant correlation i.e. between concentrations of
423 PFOA in groundwater and leachate ($R=0.74$; $p=0.014$). However, this positive
424 correlation was driven substantially by samples obtained from/near one landfill which
425 displayed the highest concentrations of PFOA in both leachate (11400 ng/L) and
426 groundwater (140 ng/L). Thus, when the correlation was examined for log-
427 transformed concentrations, it was no longer significant ($R=0.54$; $p>0.1$).

428

429 **Conclusions**

This study measured concentrations of BFRs and PFASs in air, soil, and groundwater sampled near 10 landfills in the Republic of Ireland. These were used to test the hypothesis that landfills have caused discernible contamination of their surrounding environment. Our data suggest that concentrations of BFRs and PFASs in air and soil are not discernibly impacted by emissions from the landfills studied. However, while our relatively small sample numbers prevent firm conclusions, our data suggest that leachate from landfills in this study may have some influence on concentrations of PFOA in groundwater, especially for unlined landfills. Moreover, concentrations of DBDPE in groundwater are reported for the first time anywhere and exceed those of all other BFRs and PFASs monitored in this study. Overall, our findings suggest that more detailed study of the possible impact of landfill leachate on groundwater concentrations of DBDPE, PFOA and related contaminants would appear prudent.

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References

- Abdallah, M.A., Harrad, S., Ibarra, C., Diamond, M., Melymuk, L., Robson, M., Covaci, A., 2008, Hexabromocyclododecanes In Indoor Dust From Canada, the United Kingdom, and the United States, *Environ*. *Sci*. *Technol*. 42, 459-464.
- Abdallah, M.A., Drage, D.S., Sharkey, M., Berreheim, H., Harrad, S., 2017, A rapid method for the determination of brominated flame retardant concentrations

454 in plastics and textiles entering the waste stream. *Journal of Separation Science*,
455 40, 3873-3881

456 ▪ Atkinson, C., Blake, S., Hall, T., Rumsby, P., Kanda, R. 2008. Survey of the
457 Prevalence of Perfluorooctane Sulphonate (PFOS), Perfluorooctanoic Acid
458 (PFOA) and Related Compounds in Drinking Water and Their Sources. Water
459 Research Centre, Marlow, U.K. Drinking Water Inspectorate Report DWI
460 70/2/212 (available at http://dwi.defra.gov.uk/research/completed-
461 research/2000todate.htm accessed 10th October 2019)

462 ▪ Bao, J., Yu, W-J., Liu, Y., Wang, X., Jin, Y-H., Dong, G-H. 2019. Perfluoroalkyl
463 substances in groundwater and home-produced vegetables and eggs around a
464 fluorochemical industrial park in China. *Ecotoxicology and Environmental Safety*,
465 171, 199-205.

466 ▪ BiPRO, 2011, Final Report "Study on waste related issues of newly listed POPs
467 and candidate POPs"
468 http://ec.europa.eu/environment/waste/studies/pdf/POP_Waste_2010.pdf accessed
469 3/5/19.

470 ▪ Danon-Schaffer, M. N. 2010. Polybrominated Diphenyl Ethers in Landfills rom
471 Electronic Waste. PhD Thesis, University of British Columbia.

472 ▪ D. S. Drage, S. Newton, C. A. de Wit, S. Harrad. 2016. Concentrations of legacy
473 and emerging flame retardants in air and soil on a transect in the UK West
474 Midlands. *Chemosphere*, 148, 195–203.

475 ▪ Drage, D. S., Sharkey, M., Abdallah, M. A-E., Berresheim, H., Harrad, S. 2018.
476 Brominated flame retardants in Irish waste polymers: Concentrations, legislative
477 compliance, and treatment options. *Sci. Tot. Environ.,* 625, 1535–1543.

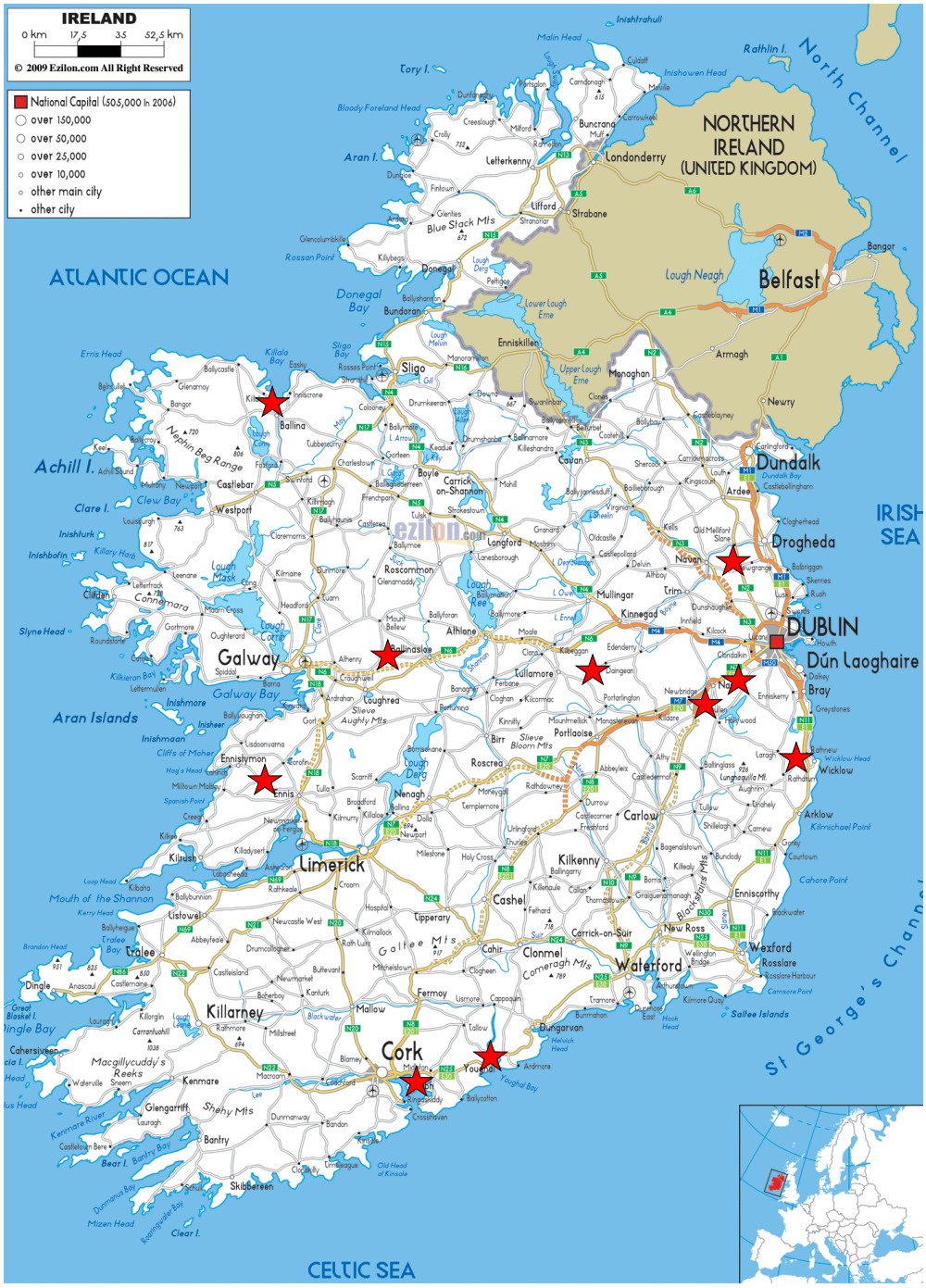
- Dreyer, A. K., Matthias, V., Temme C, Ebinghaus R. 2009. Annual time series of air concentrations of polyfluorinated compounds. Environ Sci Technol 43:4029–36.
- EC (European Commission) 2003. Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE) - Joint declaration of the European Parliament, the Council and the Commission relating to Article 9 - https://eur-lex.europa.eu/eli/dir/2002/96/oj accessed 3/5/19.
- Eschauzier, C., Raat, K. J., Stuyfzand, P. J., De Voogt, P. 2013. Perfluorinated alkylated acids in groundwater and drinking water: Identification, origin and mobility. Science of the Total Environment 458–460 477–485.
- Goosey, E. R. 2010. Towards Understanding the Fate of Perfluoroalkyl Compounds (PFCs) within Urban Environments: Implications for Human Exposure. PhD Thesis, University of Birmingham. (available at https://etheses.bham.ac.uk/id/eprint/1052/ accessed 10th October 2019).
- Goosey, E., Harrad, S. 2012. Perfluoroalkyl Substances in UK Indoor and Outdoor Air: Spatial and Seasonal Variation, and Implications for Human Exposure. *Environment International* 45, 86–90.
- Groffen, T., Rijnders, J., Verbrigghe, N., Verbruggen, E., Prinsen, E., Eens, M., Bervoets, L. 2019. Influence of soil physicochemical properties on the depth profiles of perfluoroalkylated acids (PFAAs) in soil along a distance gradient from a fluorochemical plant and associations with soil microbial parameters. *Chemosphere* 236, 124407.

- Harrad, S., Abdallah, M. A., Rose, N. L., Turner, S. D., Davidson, T. A. 2009. Current-Use Brominated Flame Retardants in Water, Sediment, and Fish from English Lakes. *Environmental Science and Technology*, 43, 9077–9083.
- Harrad, S., Drage, D. S., Sharkey, M., Berresheim, H. 2019a. Brominated flame retardants and perfluoroalkyl substances in landfill leachate from Ireland. *Science of the Total Environment* 695, 133810.
- Harrad, S., Wemken, N., Drage, D.S., Abdallah, M. A-E. Coggins, A.M. 2019b. Perfluoroalkyl Substances in Drinking Water, Indoor Air and Dust from Ireland: Implications for Human Exposure, Environ. Sci. Technol.
- Hoh, E., Hites, R.A. 2005. Brominated Flame Retardants in the Atmosphere of the East-Central United States. Environ. Sci. Technol. 39, 7794-7802.
- Hoh, E., Zhu, L. Hites, R.A. 2005. Novel Flame Retardants, 1,2-Bis(2,4,6-tribromophenoxy)ethane and 2,3,4,5,6-Pentabromoethylbenzene, in United States' Environmental Samples. Environ. Sci. Technol. 39, 2472-2477.
- Lee, S. C., Sverko, E., Harner, T., Pozo, K., Barresi, E., Schachtschneider, J., Zaruk, D., DeJong, M., Narayan, J. 2016. Retrospective analysis of “new” flame retardants in the global atmosphere under the GAPS Network. *Environmental Pollution* 217, 62-69.
- Levison, J., Novakowski, K., Reiner, E. J., Kolic, T. 2012. Potential of groundwater contamination by polybrominated diphenyl ethers (PBDEs) in a sensitive bedrock aquifer (Canada). *Hydrogeology Journal*, 20, 401–412.
- Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M., Gawlik, B.M. 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Research, 44, 4115-4126.

- Miralles-Marco, A., Harrad, S. Perfluorooctane sulfonate: A review of human exposure, biomonitoring and the environmental forensics utility of its chirality and isomer distribution. *Environ Int*., 77, 148–159 (2015).
- Murakami, M., Kuroda, K., Sato, N., Fukushi, T., Takizawa, S., Takada, H. 2009. Groundwater pollution by perfluorinated surfactants in Tokyo. Environ. Sci. Technol. 43, 3480–3486
- Newton, S., Sellström, U., de Wit, C. A. 2015. Emerging Flame Retardants, PBDEs, and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden. Environ. Sci. Technol. 2015, 49, 2912−2920.
- Rauert, C., Schuster, J. K., Eng, A., Harner, T. 2018. Global Atmospheric Concentrations of Brominated and Chlorinated Flame Retardants and Organophosphate Esters, Environ. Sci. Technol. 52, 2777−2789.
- Rankin, K., Mabury, S. A., Jenkins, T. M., Washington, J. W. 2016. A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence. Chemosphere 161, 333-341.
- Shoeib, M., Harner, T., Webster, G. M., Lee, S. C. 2011. Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: implications for human exposure. Environ Sci Technol 45, 7999–8005.
- St-Amand, A., Mayer, P., Blais, J., 2008. Seasonal trends in vegetation and atmospheric concentrations of PAHs and PBDEs near a sanitary landfill. Atmospheric Environment 42, 2948-2958.
- Trinh, M. M., Tsai, C. L., Chang, M. B. 2019. Characterization of polybrominated diphenyl ethers (PBDEs) in various aqueous samples in Taiwan. Science of the Total Environment 649, 388–395.

550 ▪ Wemken, N., Drage, D. S., Abdallah, M. A.-E., Harrad, S., Coggins, M. A. 2019.
551 Concentrations of Brominated Flame Retardants in Indoor Air and Dust from
552 Ireland Reveal Elevated Exposure to Decabromodiphenyl Ethane. *Environmental*
553 *Science and Technology*, 53, 9826−9836.
554 ▪ Weinberg, I., Dreyer, A., Ebinghaus, R. 2011. Landfills as sources of
555 polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances
556 to ambient air. Atmospheric Environment 45, 935-941.
557 ▪ Weiss, O., Wiesmüller, G.A., Bunte, A., Göen, T., Schmidt, C. K. Wilhelm, M.,
558 Hölzer, J. 2012. Perfluorinated compounds in the vicinity of a fire training area –
559 Human biomonitoring among 10 persons drinking water from contaminated
560 private wells in Cologne, Germany. International Journal of Hygiene and
561 Environmental Health 215, 212– 215.

562 **Figure 1: Locations (Denoted by Stars) of Landfills Sampled in this Study**



563

564 **Table 1: Summary[a,b] of Concentrations (pg m^{-3}) of Selected BFRs and PFASs in Air from Locations Downwind and Upwind of Irish**

565 **Landfills and Comparison with Concentrations Reported in Selected Other Studies**

Parameter (Source)	BDE-47	BDE-209	ΣHBCDD	PFOA	PFOS	PFNA	PFBS	PFHxS
Range (Downwind, This Study)	<0.1-0.32	<0.5-9.2	<0.05-3.6	4.4-97	0.23-4.3	0.08-0.52	<0.15-1.4	<0.15-0.79
Median (Downwind, This Study)	0.22	6.0	<0.05	23	1.6	0.17	0.35	0.23
Arithmetic Mean (Downwind, This Study)	0.20	6.6	0.62	33	1.7	0.23	0.50	0.34
Range (Upwind, This Study)	<0.1-0.4	<0.5-8.3	<0.05-6.1	2.7-59	<0.2-2.7	<0.08-0.31	<0.15-1.2	<0.15-0.81
Median (Upwind, This Study)	0.20	5.5	0.07	16	0.60	0.13	0.26	0.08
Arithmetic Mean (Upwind, This Study)	0.20	5.9	1.2	21	0.91	0.15	0.34	0.23
Range (Indoor air, homes, Ireland, Wemken et al, 2019; Harrad et al, 2019b)	<0.43-28	<7.5-5500	0.9-2500	<0.3-390	<0.4-210	<0.3-13	<0.4-270	<0.4-4.6
Range (n=4, Malin Head, Ireland, 2005-06, Lee et al, 2016)	-	-	<0.1-4.6	-	-	-	-	-
Range (n=4, Malin Head, Ireland, 2014, Rauert et al, 2018)	<2	<1	<0.09	-	-	-	-	-
Range of arithmetic means (UK West Midlands, Drage et al, 2016)	1.6-7.9	92-370	64-130	-	-	-	-	-
Range (Birmingham, UK, Goosey and Harrad, 2012)	-	-	-	<1.9–20	<1.0–6.1			< 1.1–30
Range (Stockholm, Sweden, Newton et al, 2015)	0.19-2.4	0.03-0.55	<0.03-0.58	-	-	-	-	-
Range (Germany, landfill locations, Weinberg et al, 2011)	<LOQ	-	-	0.2-1.2	0.23-1.3	<LOQ-0.7	<LOQ-0.46	<LOQ-0.4
Range (Germany, reference locations, Weinberg et al, 2011)	<LOQ-20	-	-	0.2-1.8	<LOQ-1.1	<LOQ-0.3	<LOQ-0.5	<LOQ-0.6
Range (Canada, Shoeib et al, 2011)	-	-	-	<0.47-9.2	<0.02	-	-	-
Arithmetic mean (Germany, Dreyer et al, 2009)	-	-	-	0.3	1.3	-	-	-
Range (USA, Hoh and Hites, 2005; Hoh et al, 2005)	2.7-41	0.2-65	0.2-9.6	-	-	-	-	-

566 [a]only those BFRs/PFASs with detection frequency ≥20 % shown

567 [b]for the purposes of calculating descriptive statistics, "not detects" replaced by 0.5 x LOD, where LOD = the detection limit

568

569 **Table 2: Summary[a] of Concentrations (pg g^{-1} dry weight) of Selected BFRs (pg g^{-1} organic matter in parentheses) and PFASs in Soil**

570 **from Locations Downwind (n=9[b]) and Upwind (n=7[b]) of Irish Landfills and Comparison with Concentrations Reported in Selected**

571 **Other Studies**

Parameter (Source)	BDE-47	BDE-99	BDE-153	BDE-183	BDE-209	ΣHBCDD	PFOA	PFOS	PFNA	PFBS	PFHxS
Range (Downwind, This Study)	6.33-320 (38-4100)	7.4-440 (16-5700)	<13-480 (<26-1700)	<13-750 (<26-5300)	430-63000 (1100-640000)	80-6200 (780-44000)	150-5800	2.4-140	<1.0-7.7	<0.6-44	<1.0-2.9
Median (Downwind, This Study)	77 (260)	61 (400)	13 (180)	48 (330)	5000 (18000)	560 (4500)	470	6.6	4.3	0.60	<1.0
Arithmetic Mean (Downwind, This Study)	100 (840)	180 (1300)	81 (380)	150 (950)	12000 (100000)	1700 (13000)	1100	26	4.5	5.9	0.77
Range (Upwind, This Study)	3.8-52 (20-420)	10-26 (32-260)	<13-940 (<60-13000)	<13-7300 (<78-38000)	<130-5700 (<340-53000)	<15-1500 (<90-10000)	130-7800	3.7-2000	2.9-33	<0.6-2.9	<1.0-3.7
Median (Upwind, This Study)	14 (140)	14 (96)	<13 (<60)	<13 (<78)	240 (1000)	180 (1200)	610	9.3	6.0	1.2	2.3
Arithmetic Mean (Upwind, This Study)	20 (170)	15 (140)	140 (1900)	1100 (5400)	1000 (10000)	520 (4400)	1600	300	14	1.1	1.8
Range (UK West Midlands, Drage et al, 2016)[c]	580-2100	550-1600	<43-440	<56-1600	940-45000	-	-	-	-	-	-
Range (Stockholm, Sweden, Newton et al, 2015)[c]	240-1700	200-1100	<33-190	-	310-31000	380-12000	-	-	-	-	-
Arithmetic mean (Canada, landfill impacted sites, Danon-Schaffer, 2010)	8300	12000	5000	16000	62000	-	-	-	-	-	-

Arithmetic mean (Canada, reference sites, Danon-Schaffer, 2010)	100	54	5	15	1600	-	-	-	-	-	-
Arithmetic mean (UK, Goosey and Harrad, 2012)	-	-	-	-	-	-	1100	560	-	-	14
Range of arithmetic means (Belgium, Groffen et al, 2019)	-	-	-	-	-	-	<130-1500	<670-8900	-	-	-
Range (North America, Rankin et al, 2016)	-	-	-	-	-	-	22-1800	30-2000	15-1100	-	2.0-37
Range (Europe, Rankin et al, 2016)	-	-	-	-	-	-	15-2700	7.1-3100	9.1-220	-	3.3-100
Range (Near Fluorochemical Industrial Park, China, Bao et al, 2019)	-	-	-	-	-	-	1200-6300	<200-1400	<200-1100	<200-42,000	<200-950

572 [a]for the purposes of calculating descriptive statistics, "not detects" replaced by 0.5 x LOD, where LOD = the detection limit

573 [b]soil samples from 3 upwind and 1 downwind locations destroyed in transit from field to laboratory

574 [c]concentrations expressed as pg g^{-1} normalised to soil organic matter content

575 **Table 3: Summary[a] Concentrations (ng L^{-1}) of Selected BFRs and PFAS in Groundwater Samples Linked to Irish Landfills and**
576 **Comparison with Concentrations Reported in Selected Other Studies**

Parameter/Source	BDE-47	BDE-99	BDE-209	DBDPE	ΣHBCDD	PFOA	PFOS	PFBS	PFHxS	FOSA
Range (This Study)	0.17-0.57	<0.1-1.4	5.8-26	1.3-630	<0.1-2.4	1.6-96	<0.1-1.3	<0.1-0.22	<0.1-0.28	<0.1-1.0
Median (This Study)	0.28	<0.1	9.0	9.4	0.81	3.7	<0.1	<0.1	<0.1	0.11
Arithmetic Mean (This Study)	0.31	0.31	12	78	0.91	30	0.21	<0.1	<0.1	0.22
Detection frequency (%)	100	50	100	100	80	100	20	20	20	70
Range (Landfill leachate, Ireland, Harrad et al, 2019)	<0.1-140	<0.3-58	<1.0-220	-	<0.2-43	9.0-11000	<0.1-7400	<0.1-1700	<0.1-2600	<0.2-65
Range (Tapwater, Ireland, Harrad et al, 2019)	-	-	-	-	-	0.04-18	<0.15-0.76	<0.2-15	-	-
Range (Tokyo, Murakami et al, 2009)	-	-	-	-	-	0.47-60	0.3-130	-	-	<0.1-0.49
Range (UK, Atkinson et al, 2008)	-	-	-	-	-	<24-260	<11-160	-	-	-
Range (Germany, Weiss et al, 2012)	-	-	-	-	-	<LOQ-160	0.02-8400	<LOQ-100	<LOQ-2400	-
Arithmetic Mean (EU, Loos et al, 2010)	-	-	-	-	-	3.0	4.0	<0.3	1.0	-
Range (Pumping well water, the Netherlands, Eschauzier et al, 2013)	-	-	-	-	-	0.5-1.3	<0.01	<0.01	<0.22	-
Range (Taiwan, Trinh et al, 2019)	1.1-390	0.2-77	6.9-3100	-	-	-	-	-	-	-
Range (Canada, Levison et al, 2012)	<2-10	<1-7.2	<2-92	-	-	-	-	-	-	-

577 [a]only those BFRs/PFASs with detection frequency ≥20 % shown
578 [b]for the purposes of calculating descriptive statistics, "not detects" replaced by 0.5 x LOD, where LOD = the detection limit

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